# Continuous Monitoring for Nutrients:
## State of the Technology and State of the Science


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**U.S. Department of the Interior**
**U.S. Geological Survey**

# Acknowledgements

- **Contributors to this talk**
  - Brian Bergamaschi, Bryan Downing, JohnFranco Saraceno (USGS, CA Water Science Center)
  - Jennifer Graham, Guy Foster, Andy Ziegler (USGS, KS Water Science Center)
  - Ryan Jackson (USGS, IL Water Science Center)
  - Jessica Garrett, Steve Kalkhoff (USGS, IA Water Science Center)
  - Amanda Booth, Eduardo Patino (USGS, FL Water Science Center)
  - Beth Stauffer, Denise Shaw (EPA)
  - Many, many more…
- **Funding sources**
  - USGS (NAWQA, Office of Water Quality)
  - Federal and state cooperators and partners
  - Many more…

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# Continuous Monitoring

- **24/7 data collection**
- **Wide range of constituents with direct or proxy measurements**
- **Intervals of seconds to hours**
- **Capture all events**
- **Remote access and control of sensors**

*Mississippi River at Baton Rouge*

USGS

# State of the Technology

1. **Continuous water quality monitoring is not new**
   - Water temperature → turbidity are common
2. **Continuous nitrate monitoring is beyond “proof-of-concept”**
   - But not (yet) simple, cheap or easy

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*Liberty Island, CA*

# Ion Selective Electrodes (ISE)

Direct potentiometry between a sensing electrode and a reference electrode

**Advantages:**

- Inexpensive ($<1K)
- Available for nitrate and ammonium, …
- Easy to use
- Large measurement range
- Not influenced by color or turbidity

**Disadvantages:**

- Lower resolution, accuracy, and precision
- Subject to ionic interferences
- High instrument drift
- Fouling problems

*Available since the 1970s…*


USGS

# Wet Chemical Sensors

Wet chemical colorimetric reaction, detection by photometry

**Advantages:**

- High resolution, accuracy and precision
- Multiple constituents (nitrate, ammonium, orthophosphate, silica)
- Relatively fast response time
- Potential for in situ calibrations

**Disadvantages:**

- Expensive ($15-20K)
- High power requirement
- High potential for fouling
- High maintenance costs
- Requires reagents
- Generates waste

*Available since the 1980s…*

USGS

# Optical (UV) Sensors

## Spectral absorption by a photometer

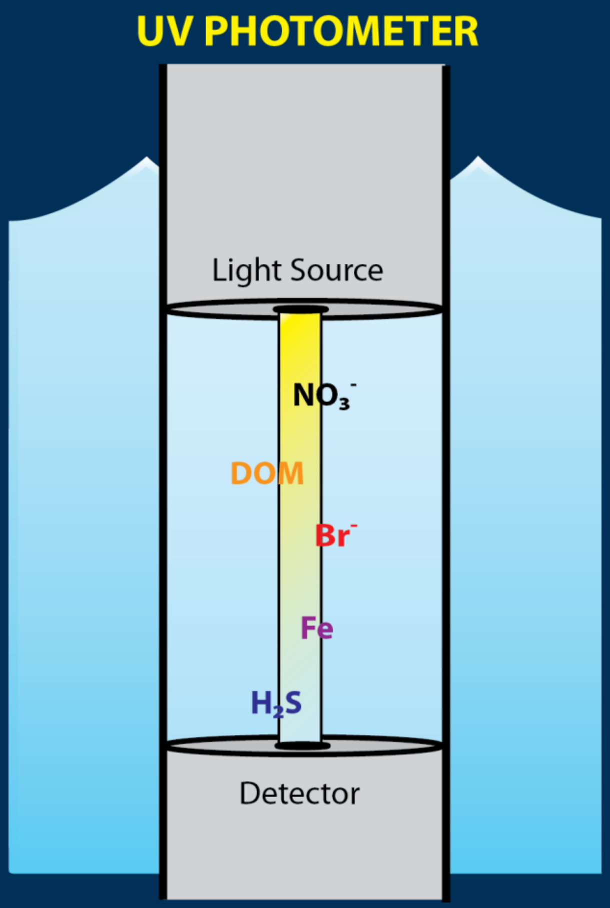
**Advantages:**

- High resolution, accuracy and precision
- Large measurement range
- Chemical-free
- Fast response time
- Additional optical information in spectra
- Anti-fouling measures

**Disadvantages:**

- Expensive ($15-25K)
- Nitrate (and nitrite) only
- High power requirement
- High maintenance costs
- Subject to a range of optical interferences

*Available since early 2000s…*

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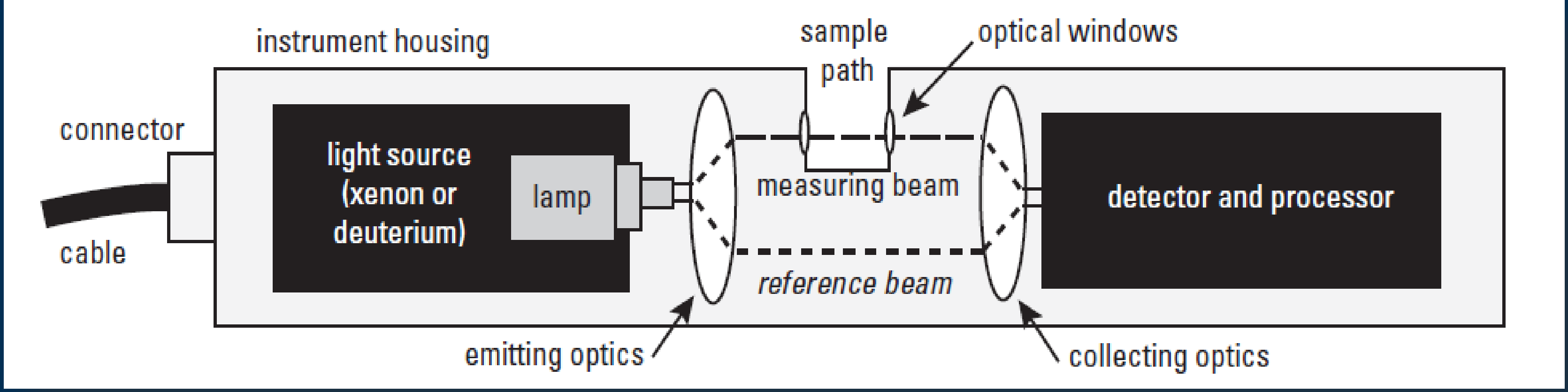
# UV Nitrate: From Lab to Field

- Spectrophotometer: Measures the intensity of light after passing through a solution
- Similar to Standard Method 4500-NO3- B (APHA, AWWA, WEF, 1995)


- *Miniaturized components*
- *Rugged housings*
- *Efficient power handling*
- *No (or few) moving parts*
- *Internal dataloggers and controllers*
- *Anti-fouling systems*
- *On-board data processing*




Pellerin et al., 2013

# Choosing a UV Nitrate Sensor

Differences affect instrument range, accuracy drift, tolerance for interferences, power consumption, field maintenance, and **COST**

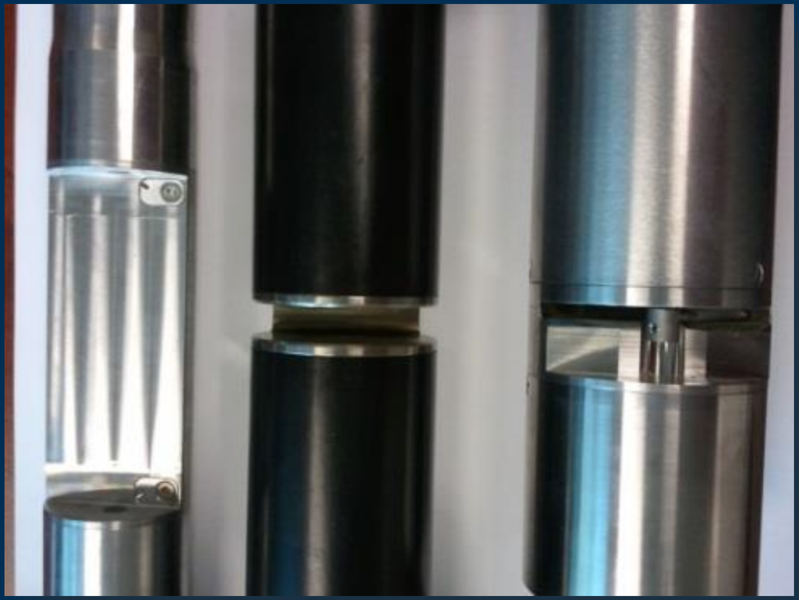
- **History** (wastewater vs. oceanography)
- **Light source** (deuterium vs. xenon flash lamp)
- **Measurement path** (path length, optical window materials)
- **Spectrophotometer** (wavelengths measured)
- **Processing algorithm** (local, global)
- **Reference detectors**
- **Anti-fouling methods** (wipers, air, copper)

Photos: http://www.mbari.org/twenty/isus.htm; www.hach-lange.co.uk

# UV Nitrate Sensor Design

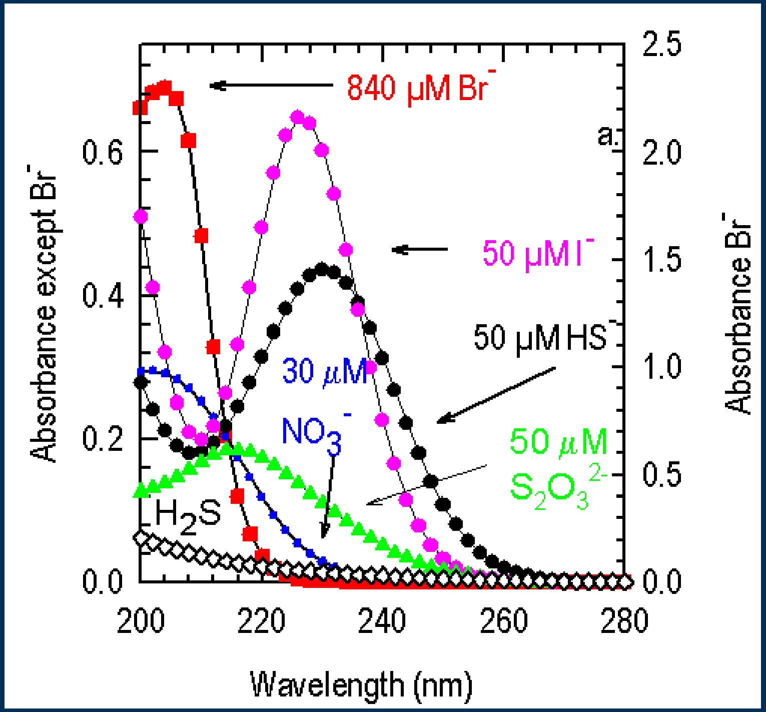
Keys for high quality UV nitrate sensor measurements:

**1) Choose appropriate path length (0.5 – 100 mm)**



35 mm 10 mm 2 mm

**2) Measure necessary wavelengths (2 – 256 UV wavelengths)**




www.mbari.org

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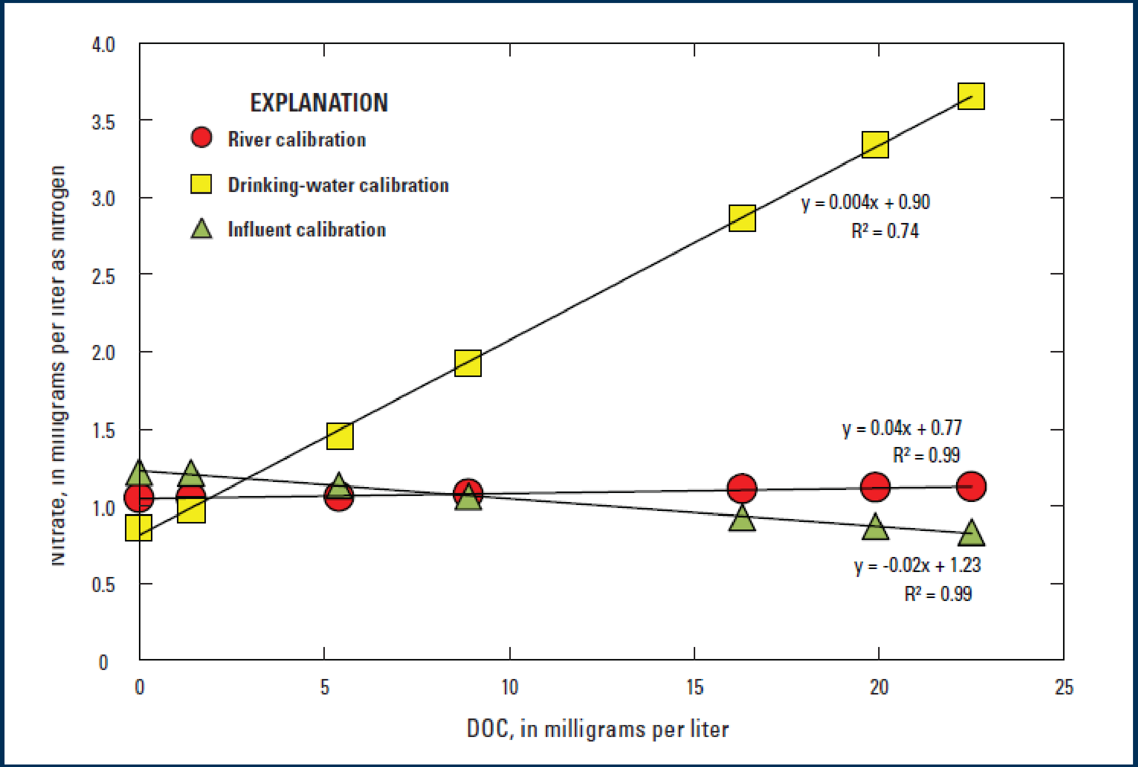
# UV Nitrate Sensor Design

## Keys for high quality UV nitrate sensor measurements:

**3) Get the right algorithm**

- **Proprietary algorithms**
  - Based on field and lab data
- **Calibration types**
  - Global
  - Application-specific (wastewater, seawater, etc.)
  - Local
- **Compensation for interferences**




Same sensor, same solution, different algorithm!

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# Anti-Fouling

- A dirty optical sensor is virtually worthless
- Wide range of anti-fouling approaches:
  - Wipers
  - Compressed air
  - Copper/biocides
  - …


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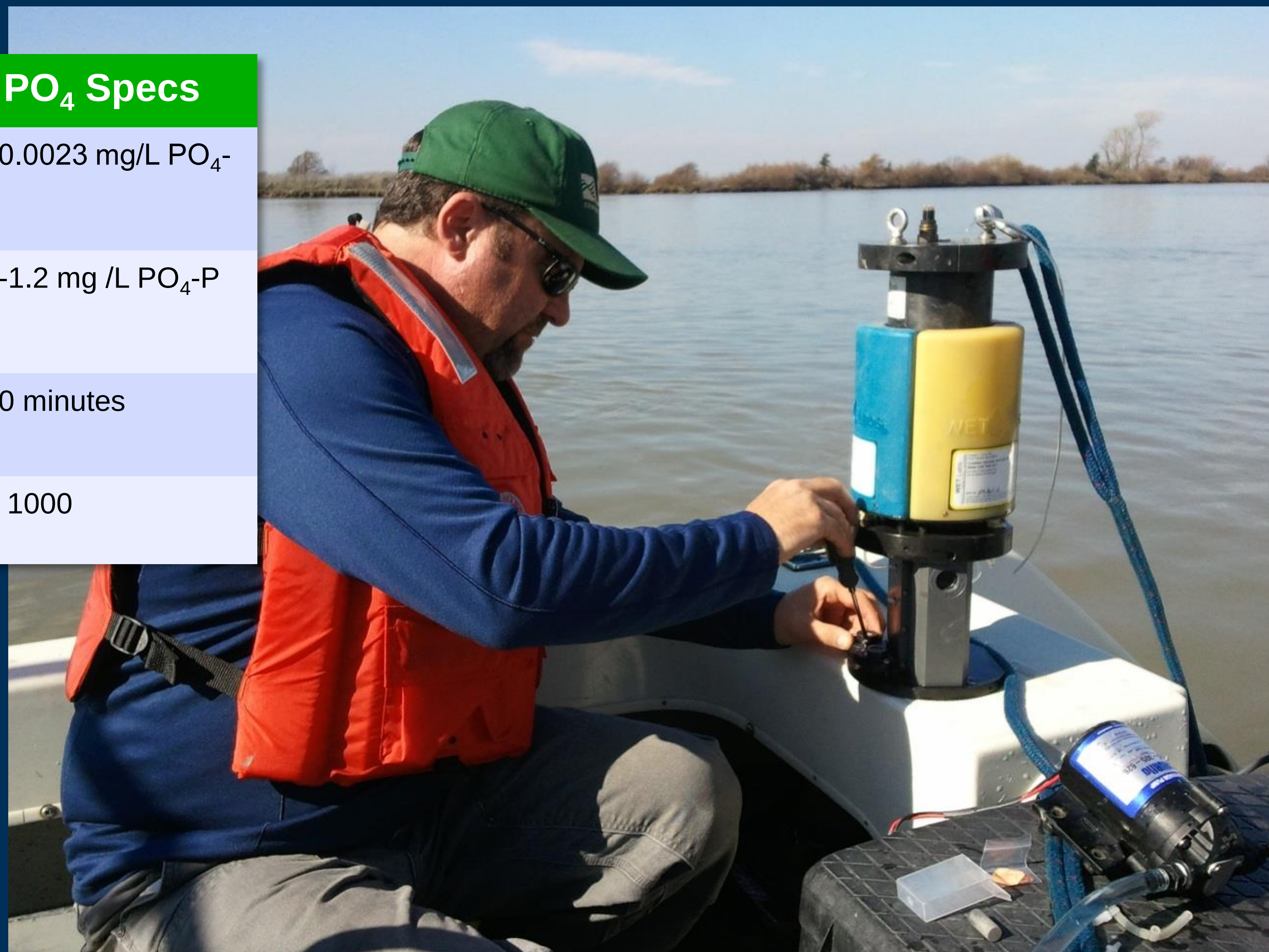
Photos: Dick Cartwright, USGS, NY Water Science Center; Joe Bell, USGS, MD Water Science Center

# Wet Chemical Nutrient Sensors

- Field deployable, wet chemical sensor using standard colorimetric methods
- Available for orthophosphate, ammonium, nitrate, and silica
- USGS operates ~5 as part of testing / “proof-of-concept” for monitoring

| Example Sensor $PO_4$ Specs | |
|---|---|
| **Detection Limit** | ≤0.0023 mg/L $PO_4$-P |
| **Maximum Concentration Range** | 0-1.2 mg /L $PO_4$-P |
| **Maximum Sampling Rate** | 30 minutes |
| **Samples Per Reagent** | ~ 1000 |



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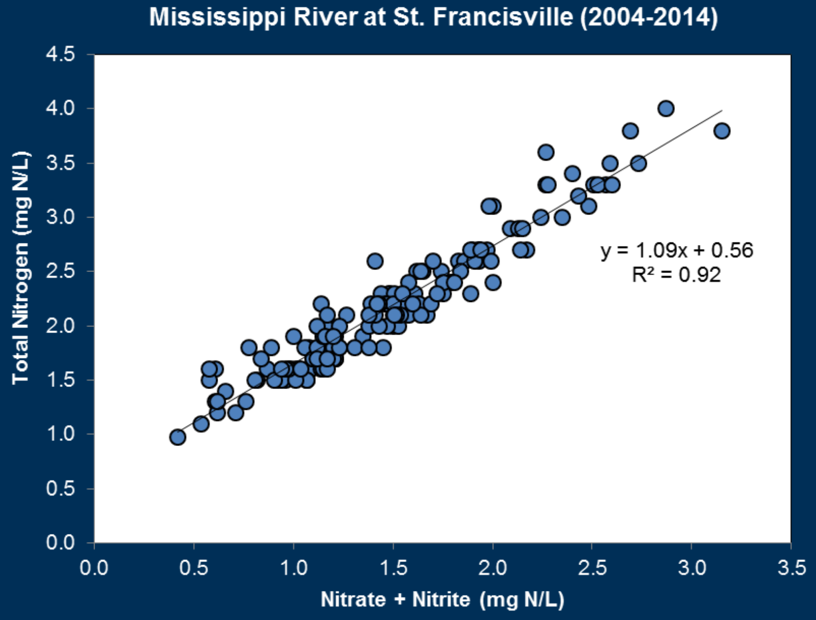
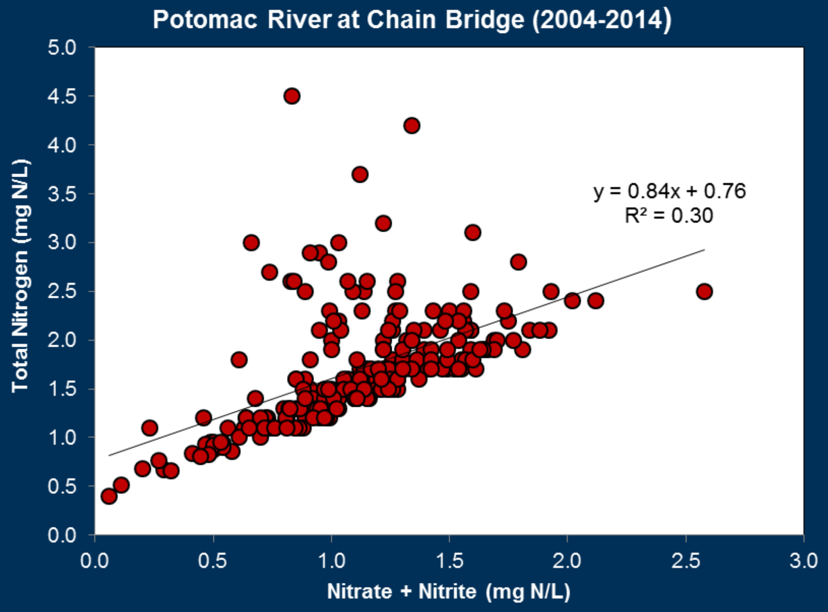
# Total Nitrogen / Phosphorus

- Standard lab methods use chemicals (alkaline persulfate oxidation) or high temperature (combustion)
- Surrogate approaches will likely be needed

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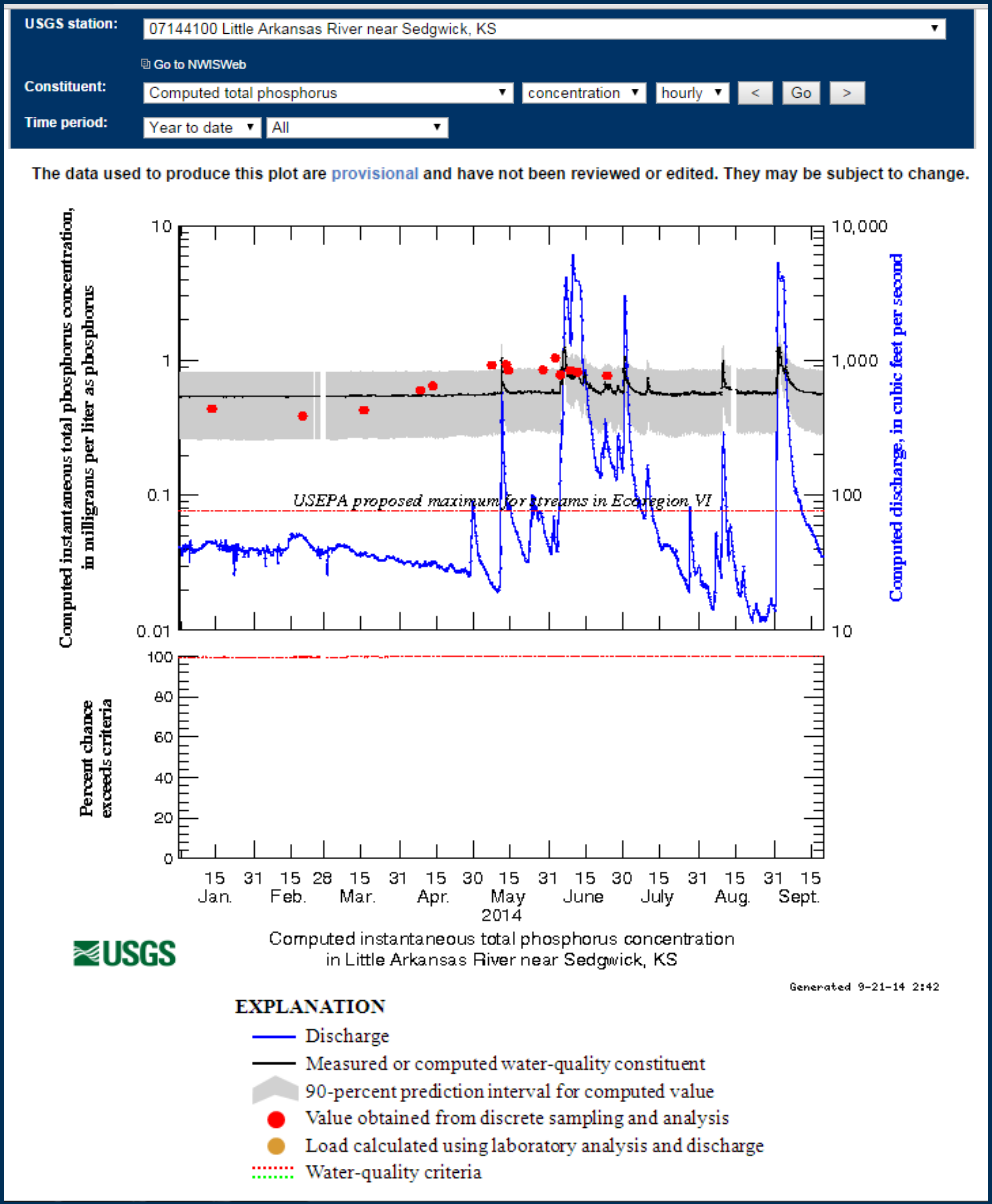
# Surrogate Approaches

- Current computed concentrations and loads using in-stream water-quality sensor measurements as surrogates for parameters that can't be measured directly

- Concentrations, loads, methods used, and models as well as published reports are available.

- Surrogate web pages: http://nrtwq.usgs.gov

*Model: TP = 0.534 + 0.00111 TURB; $r^2$ = 0.74*

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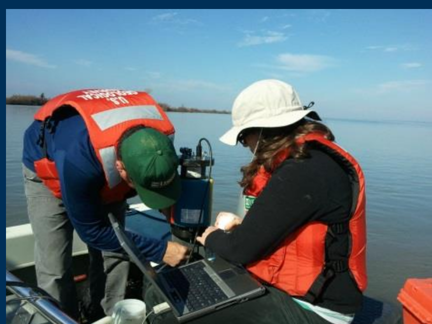
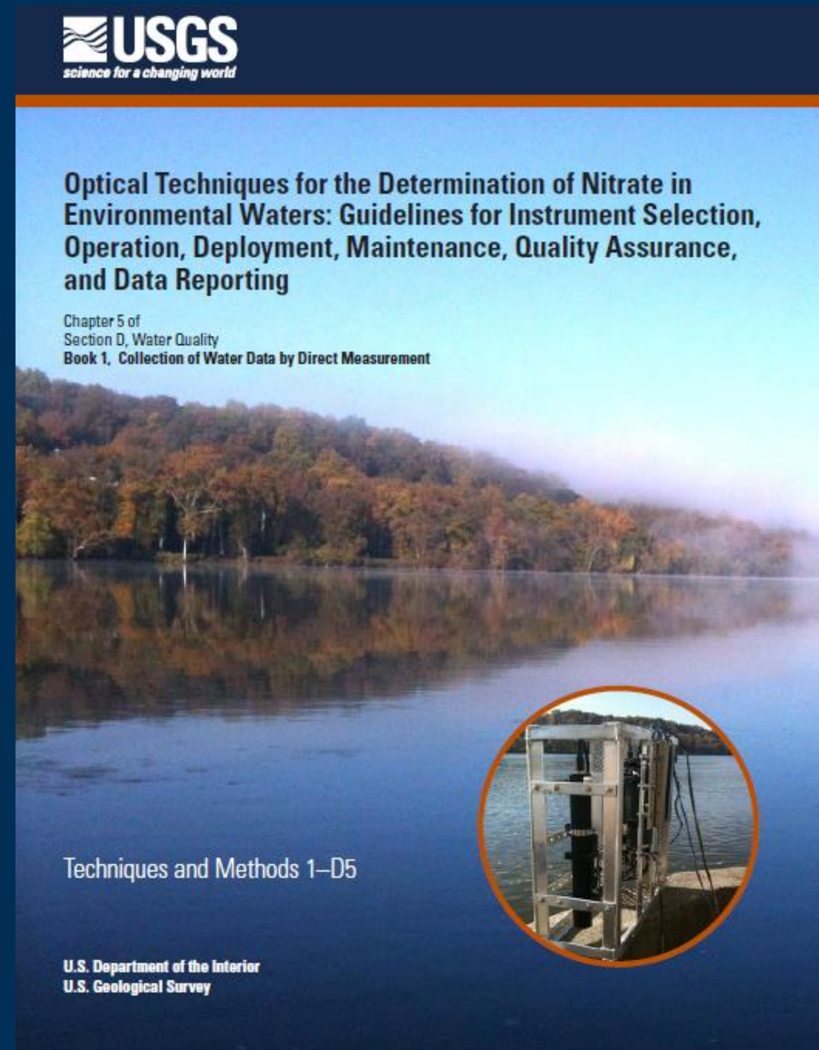
# Guidelines and Protocols

- Instrument characterization
- Guidelines for use in a range of environments
- Continued interactions with manufacturers




pubs.usgs.gov/tm/01/d5

# State of the Science

1. **Revolution:** Time dense data in real-time
2. **New opportunities for:**
   - Water quality monitoring
   - Load assessment
   - Source identification
   - Event detection
   - Aquatic processes
   - Real-time decision support
   - …

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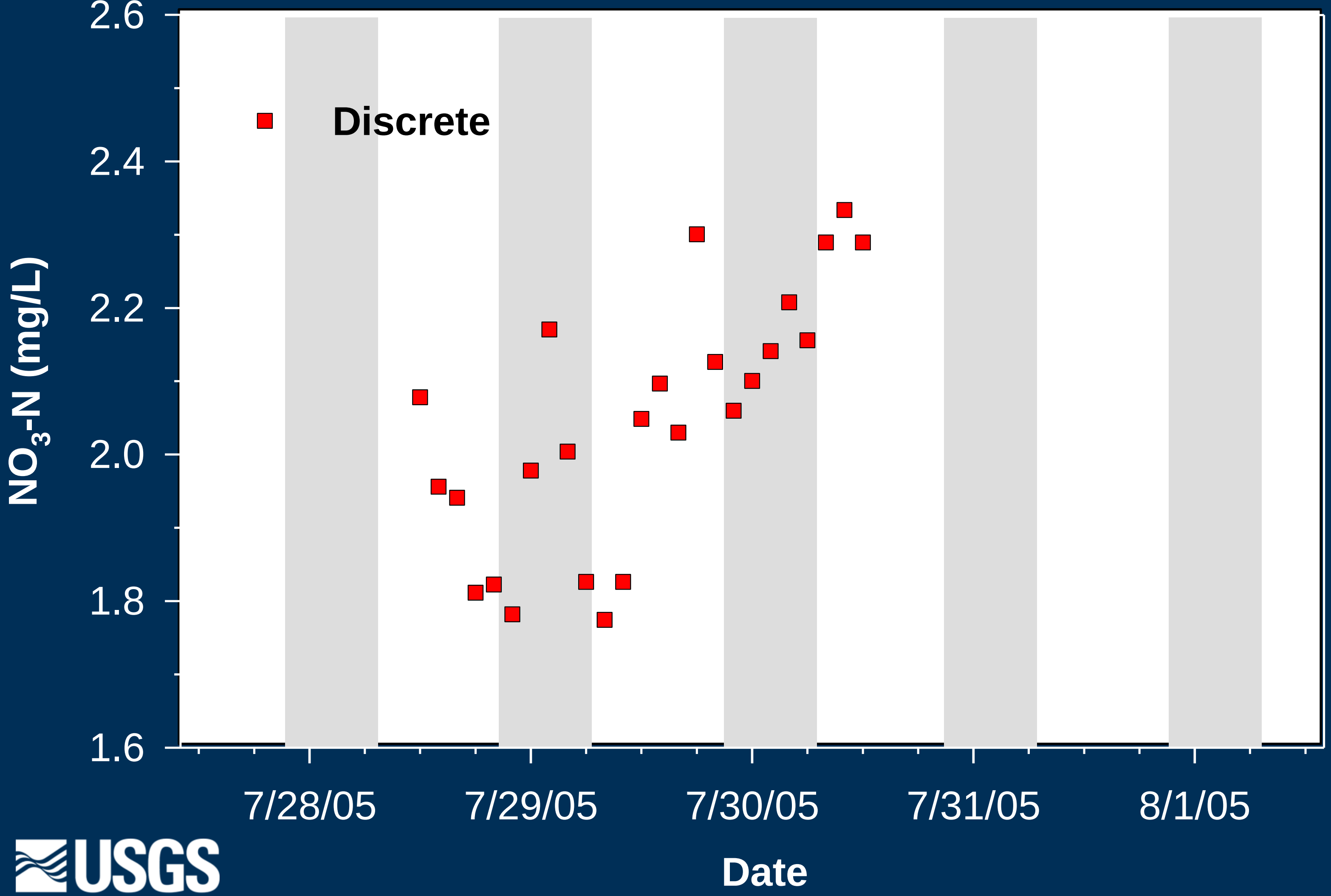
Potomac River at Little Falls

# Nitrate variability – San Joaquin River

Assessing diurnal nitrate variability in the San Joaquin River, Crows Landing, CA




Pellerin et al., 2009

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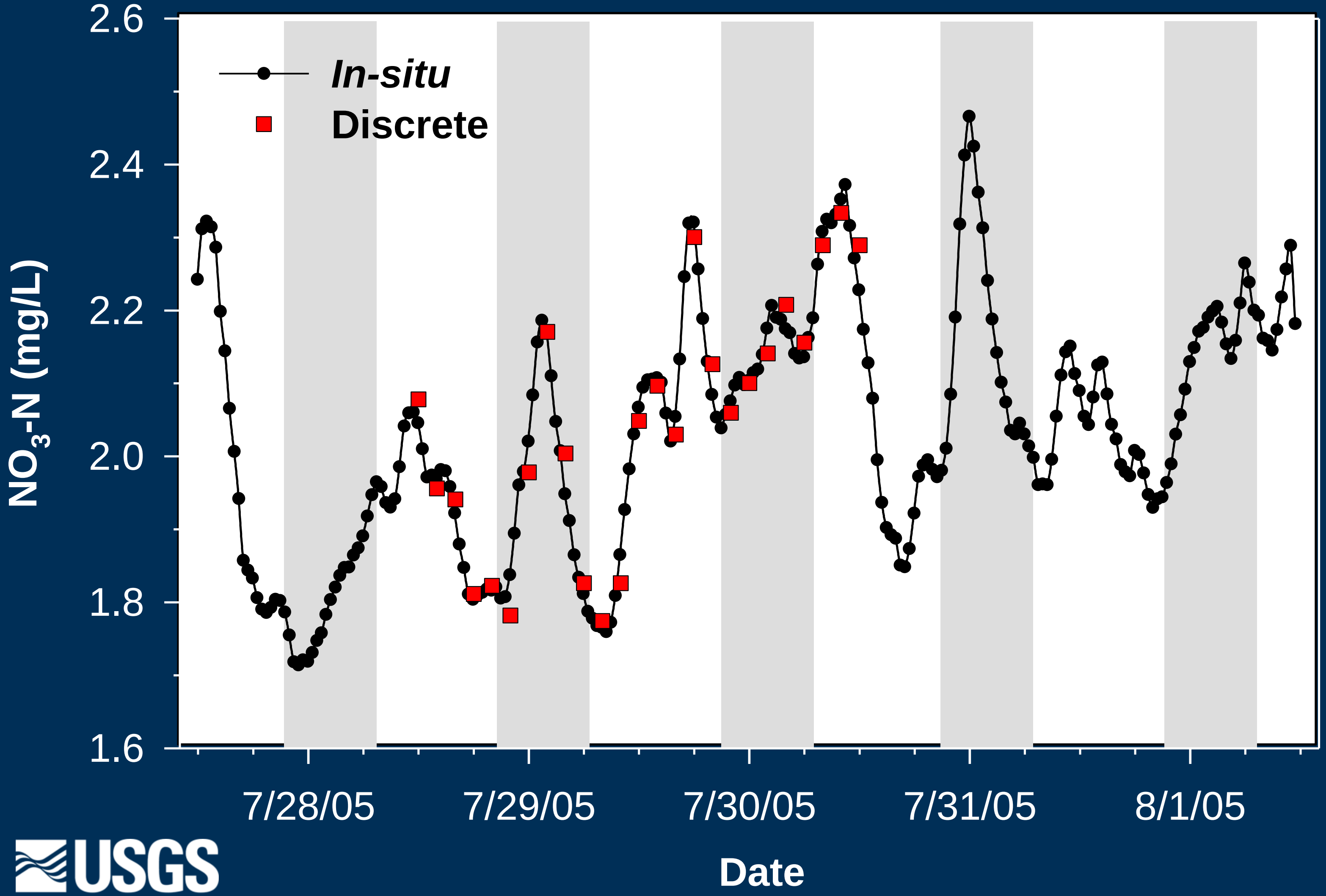
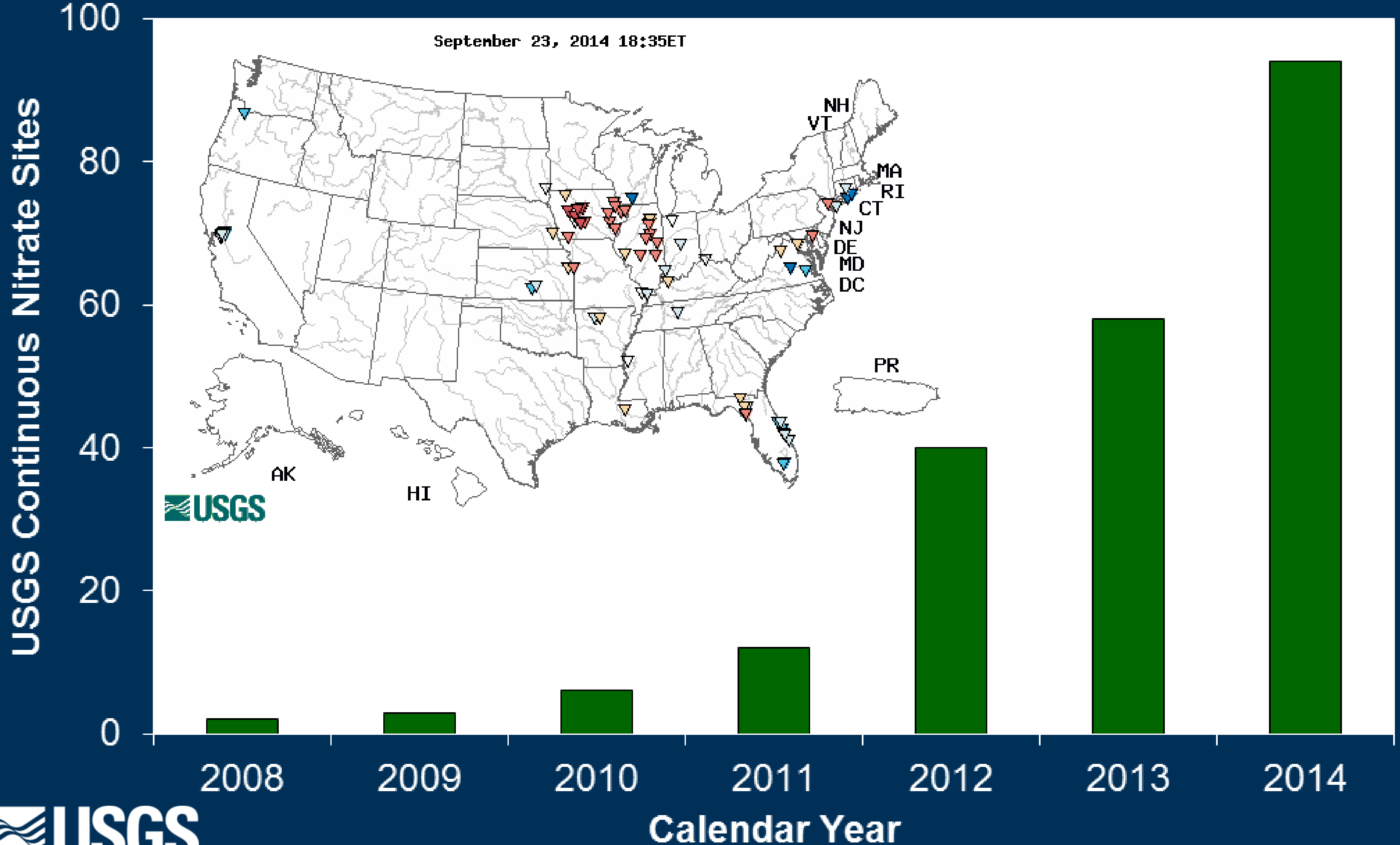



Pellerin et al., 2009

# USGS Continuous Nitrate Monitoring

- 96 sites nationwide (operated in 24 states)
- Extensive network in the Mississippi River Basin
- Most nitrate monitoring funded by cooperators (several sites threatened)

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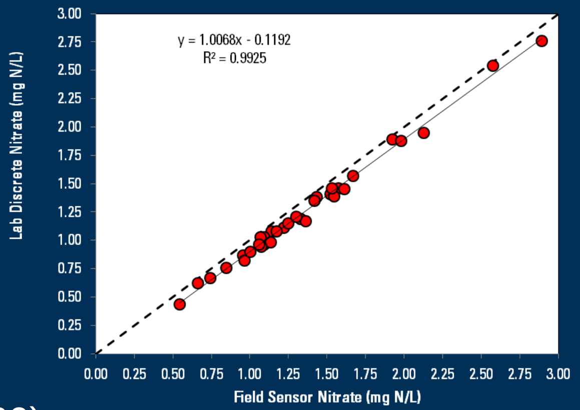
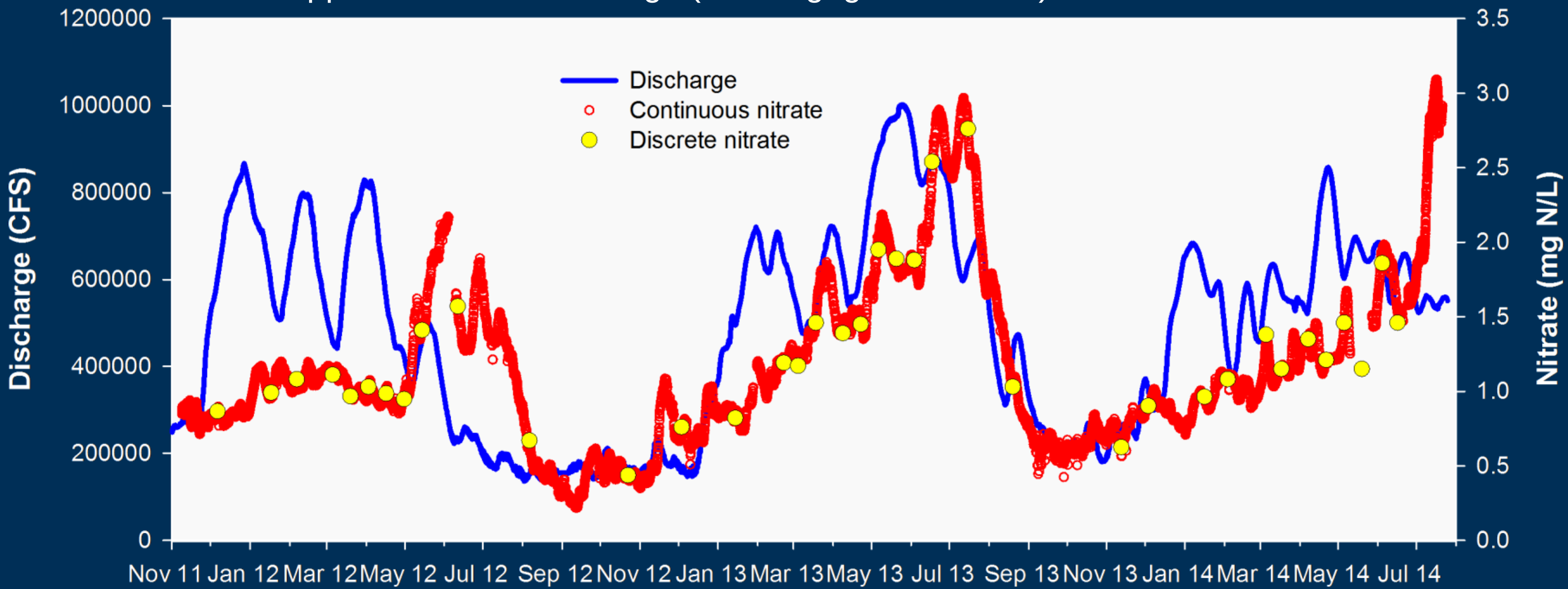
Real-time map at http://waterwatch.usgs.gov/wqwatch/

# Mississippi River Nitrate

- Strong correlation between in situ and discrete nitrate (depth- and width-integrated)
- Nitrate "flush" in spring 2013 (following 2012 drought)
- Dynamic nature, not well correlated with Q
- Estimated error ~ ± 4%

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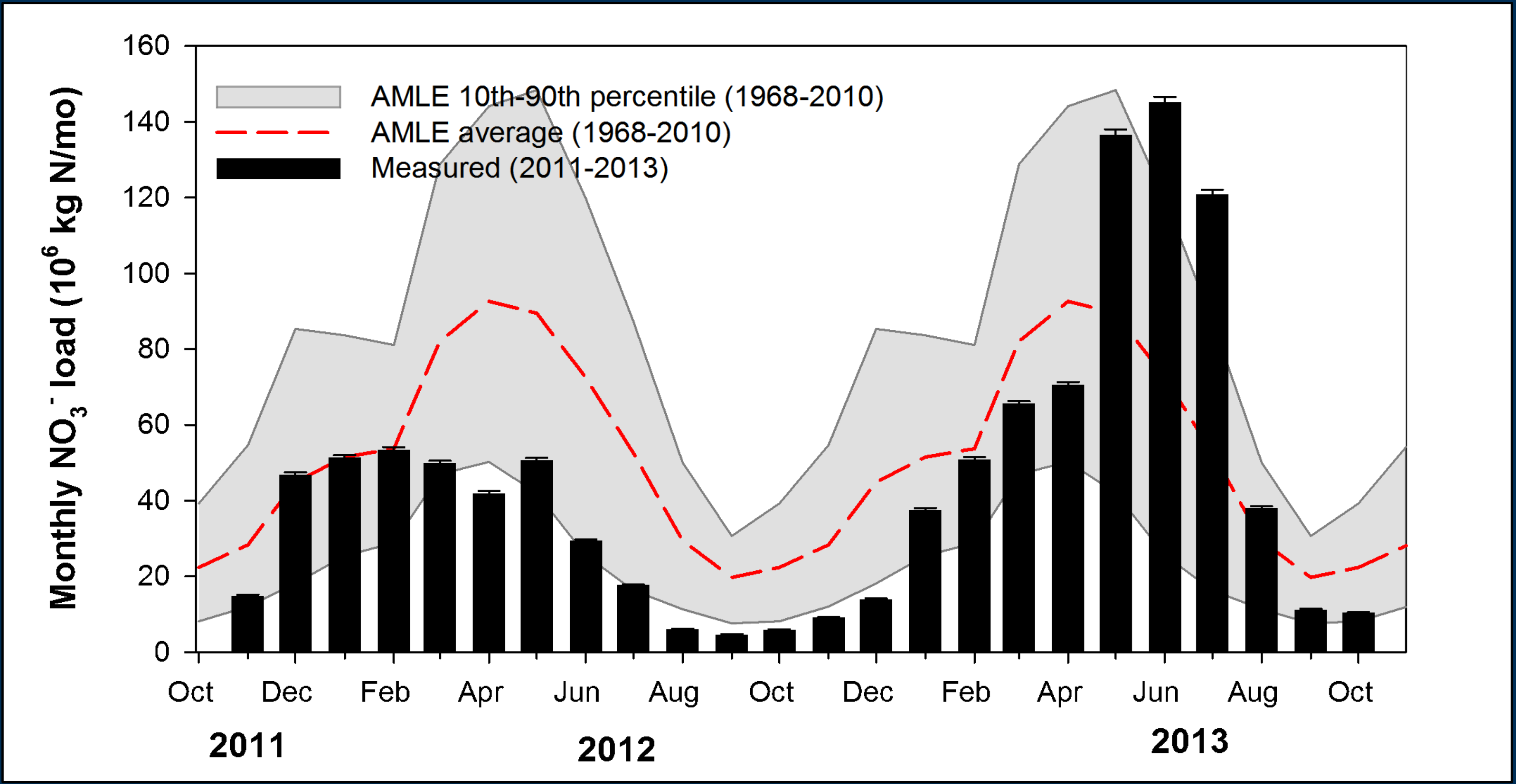
Pellerin et al., in review

# Can we improve load estimates?

- Differences in modeled vs. sensor loads of up to 30% in the spring (sensor > model)
- Order of magnitude lower uncertainty in the sensor vs. model loads
- Loads below the 10th and above the 90th percentiles during this period




*(Pellerin et al., in review)*

LOADEST data from St. Francisville, continuous data from Baton Rouge;
http://toxics.usgs.gov/hypoxia/mississippi/flux_ests/delivery/index.html; * http://www.gulfhypoxia.net/

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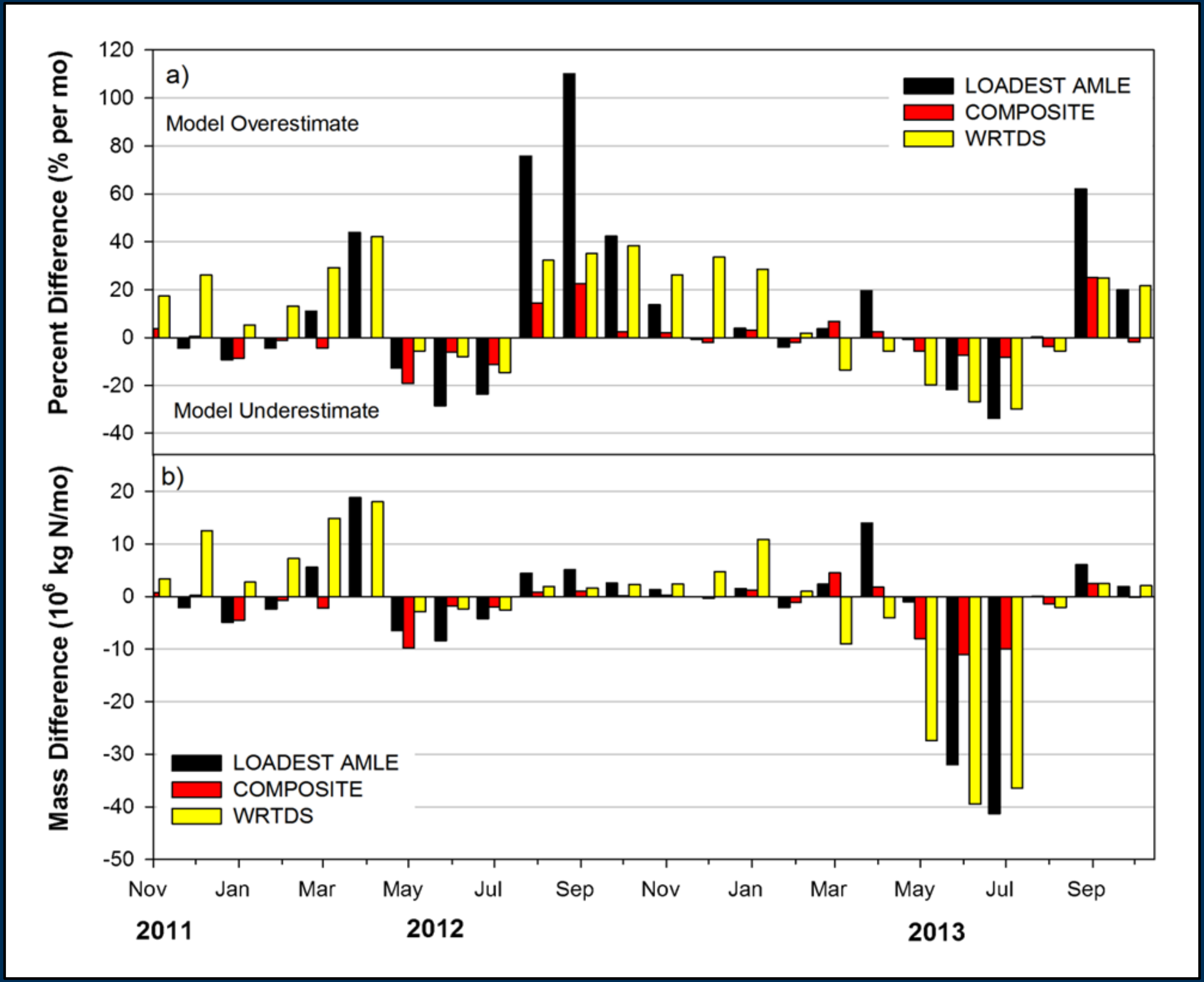


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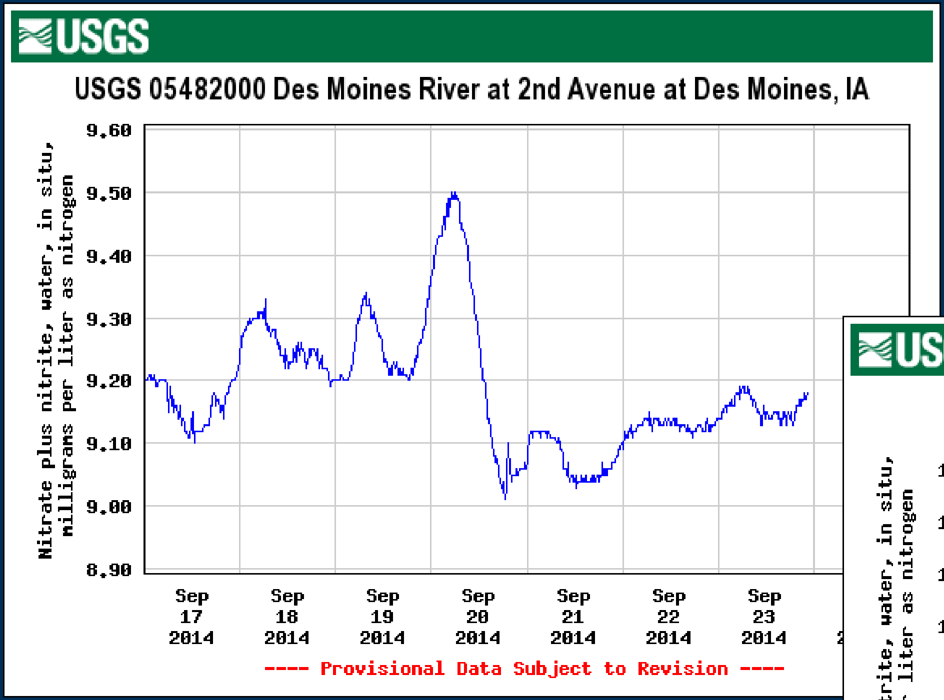
(Pellerin et al., in review)

# Real-Time Management

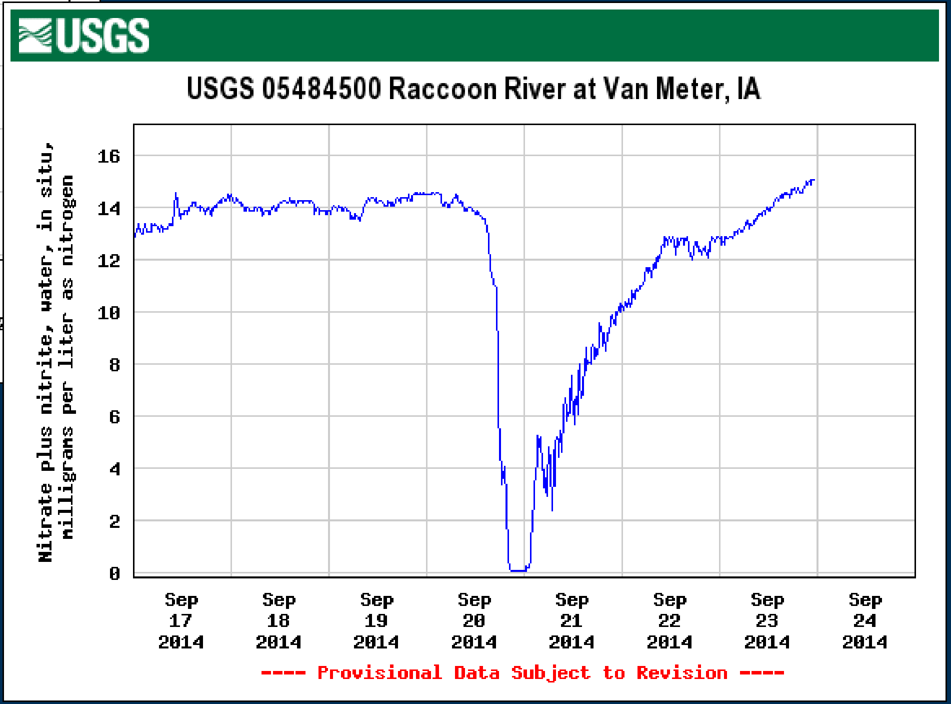
**"Record nitrate levels in Raccoon, Des Moines threaten Des Moines-area tap water"** - *Des Moines Register* (May 10,2013)




Courtesy: Jessica Garrett, USGS, IA

Des Moines Water Works nitrate removal system:

- $4 million installation (1992)
- $7,000 per day to operate



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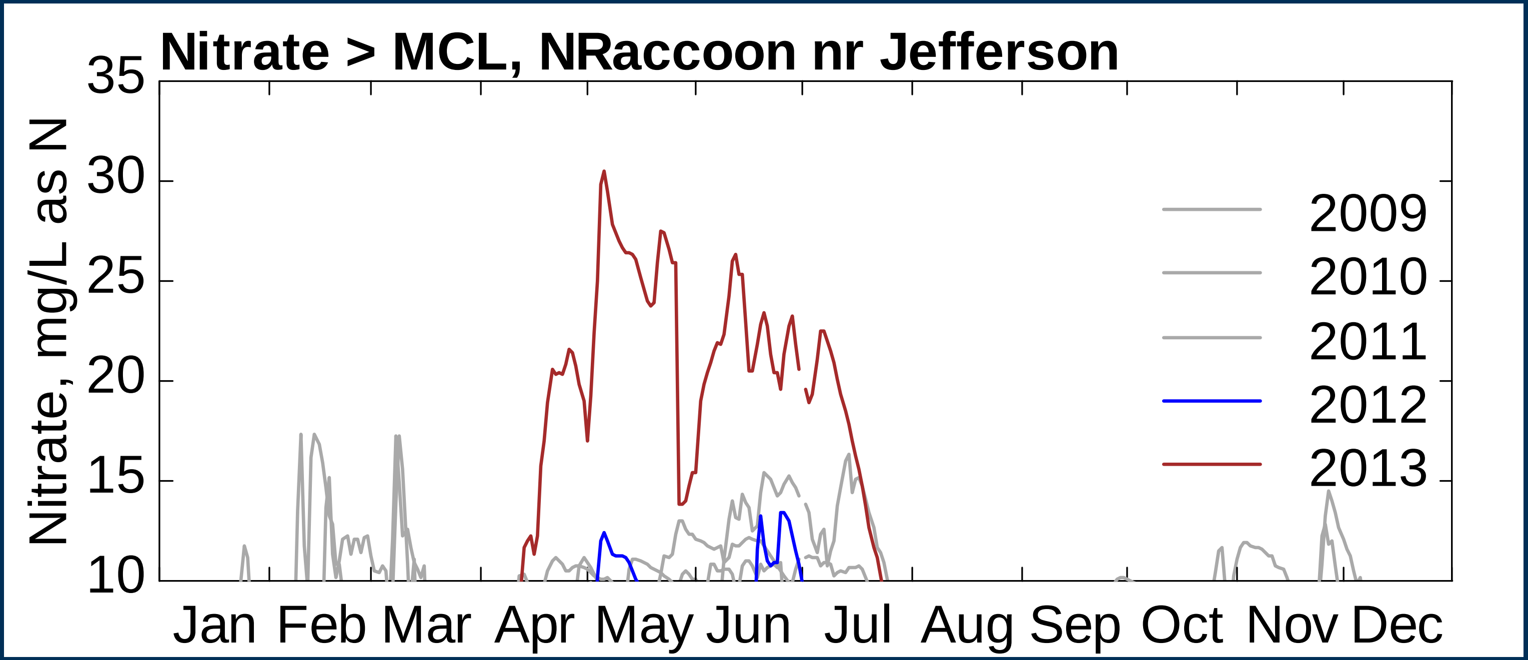
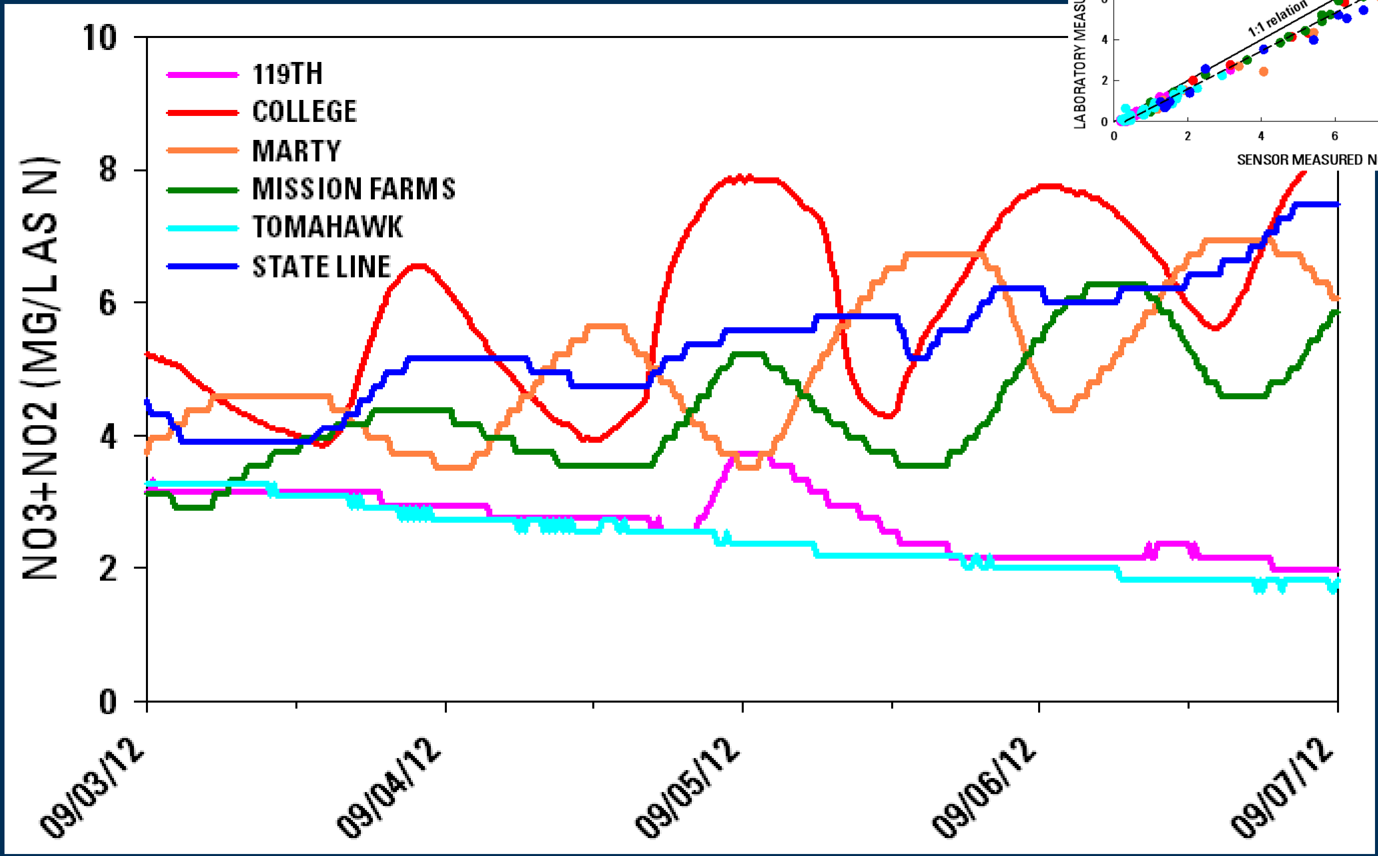
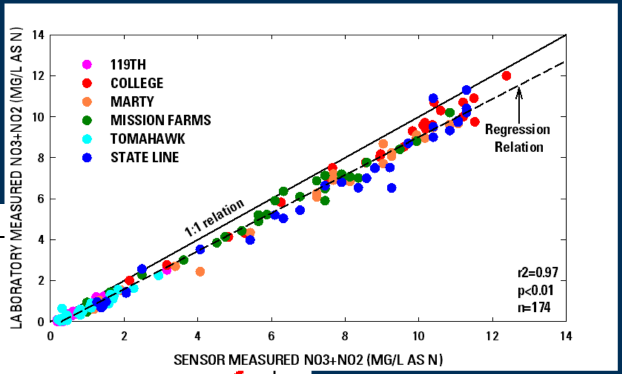



Courtesy: Jessica Garrett, USGS, IA

# Diurnal Variability in Indian Creek, KS

Diel variability in nitrate concentrations was highest immediately downstream a WWTF (College site) and lowest at the upstream sites.




Jennifer Graham, USGS, KS

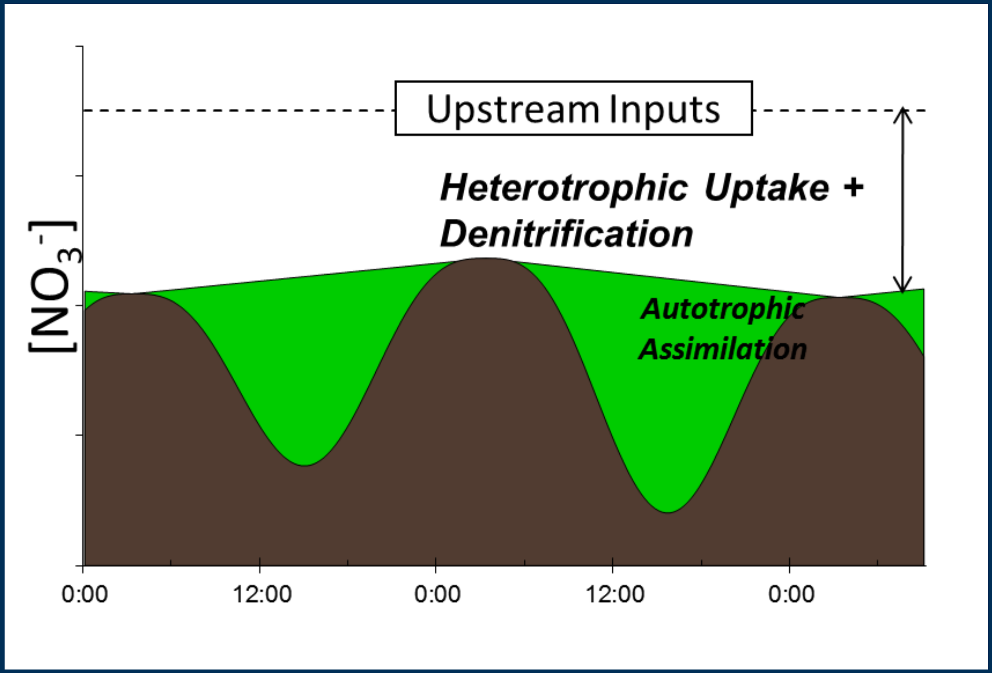
# Aquatic N Metabolism

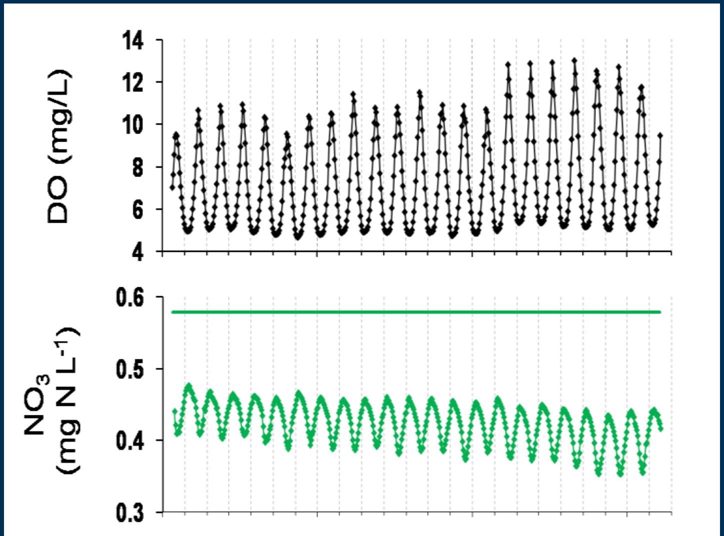
Application of nitrate sensors to understand how rivers transform and transport nitrogen in Ichetuknee Spring, Florida

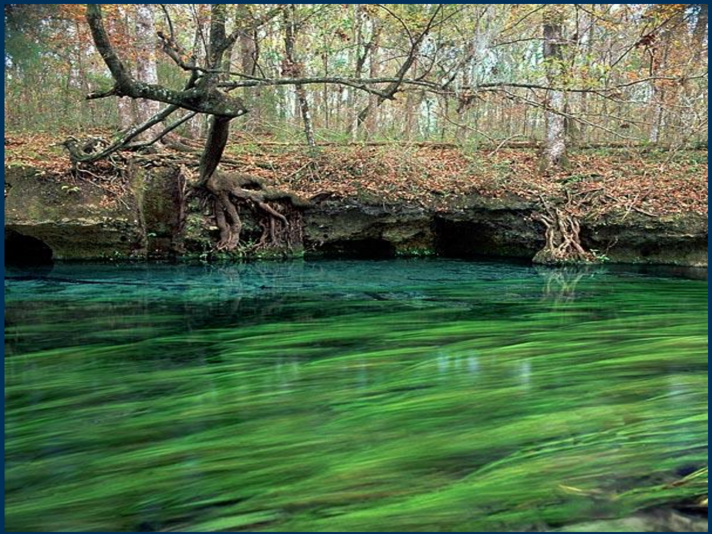
Upstream [$NO_3$] constant

Integrated diel [$NO_3$] variation = uptake ($U_a$)

Total removal yields denitrification ($U_{den}$) by difference



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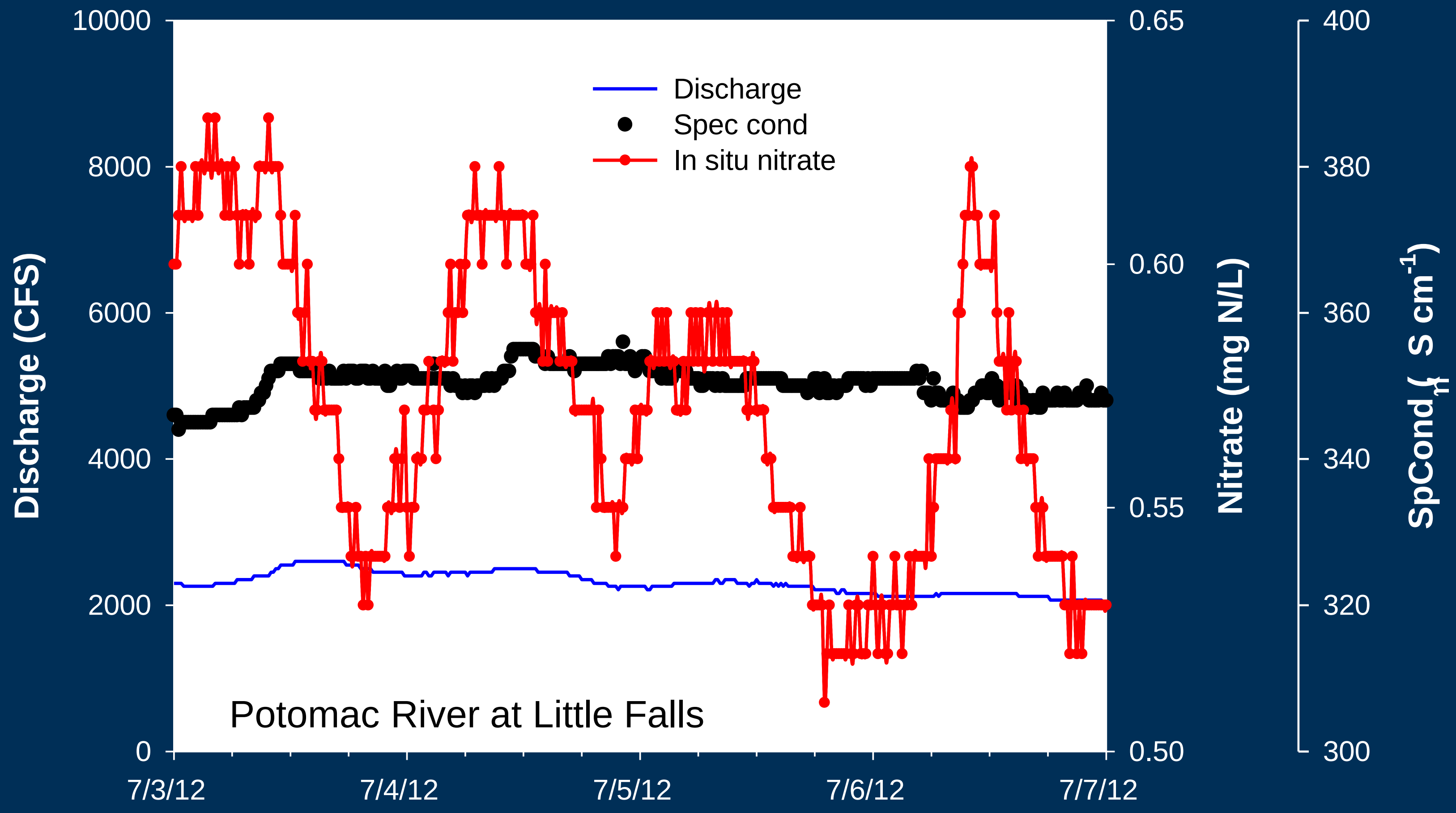
Heffernan and Cohen, 2010

# Estimating Aquatic N Retention

- Refine modeled aquatic N decay terms (e.g. SPARROW)
- Help with estimating groundwater N loading?

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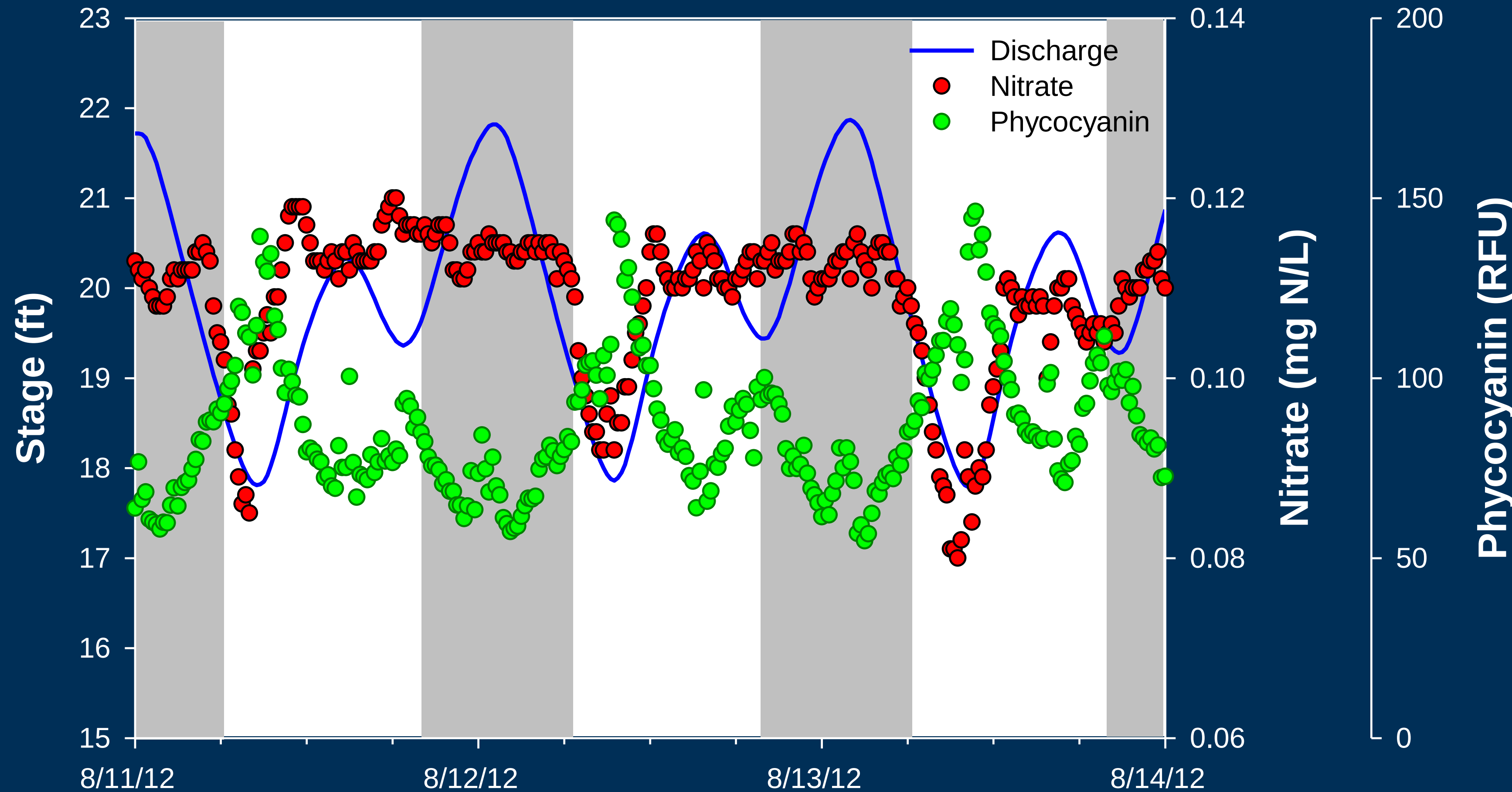
# Drivers of N Uptake

Evidence for draw down of N (and P) to support algal production?

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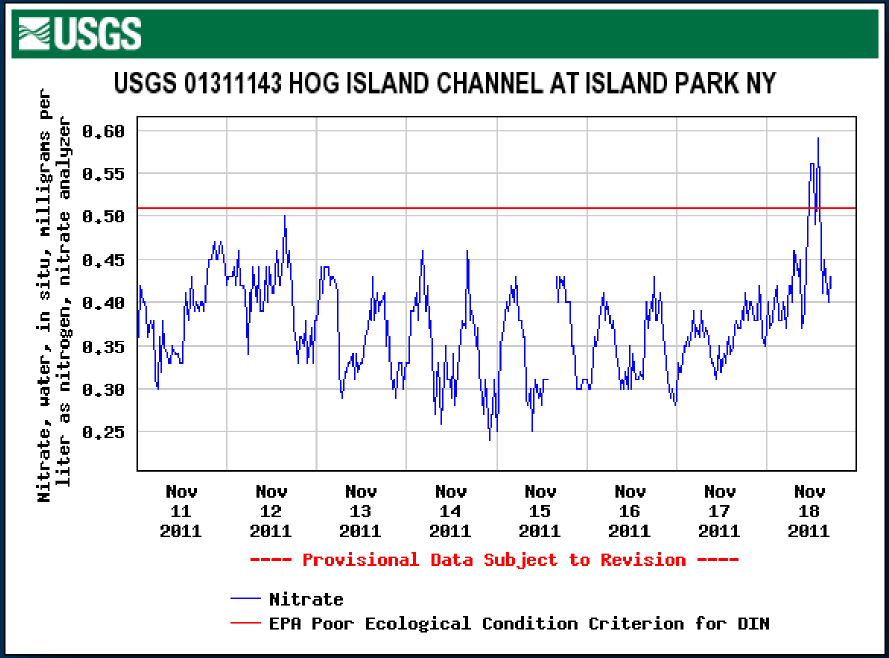
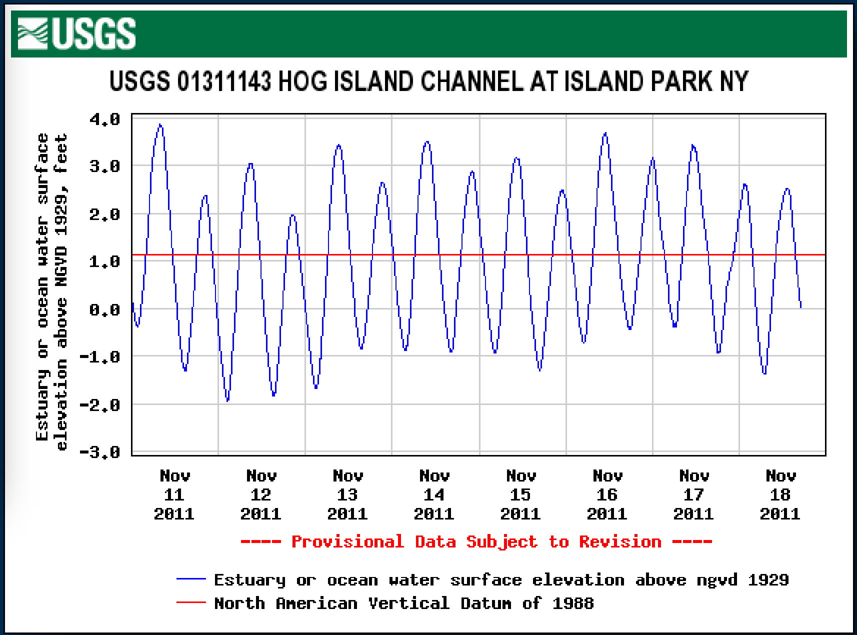
Liberty Island, CA Bay Delta

# Nitrate Variability in Tidal Environments

- Commonly exhibits semi-diurnal fluctuations
- $NO_3^-$ peaks at times of low tide and salinity minima
- Frequent inverse relation with salinity suggests dominant source is primary input(s) of freshwater








Dick Cartwright, USGS, NY

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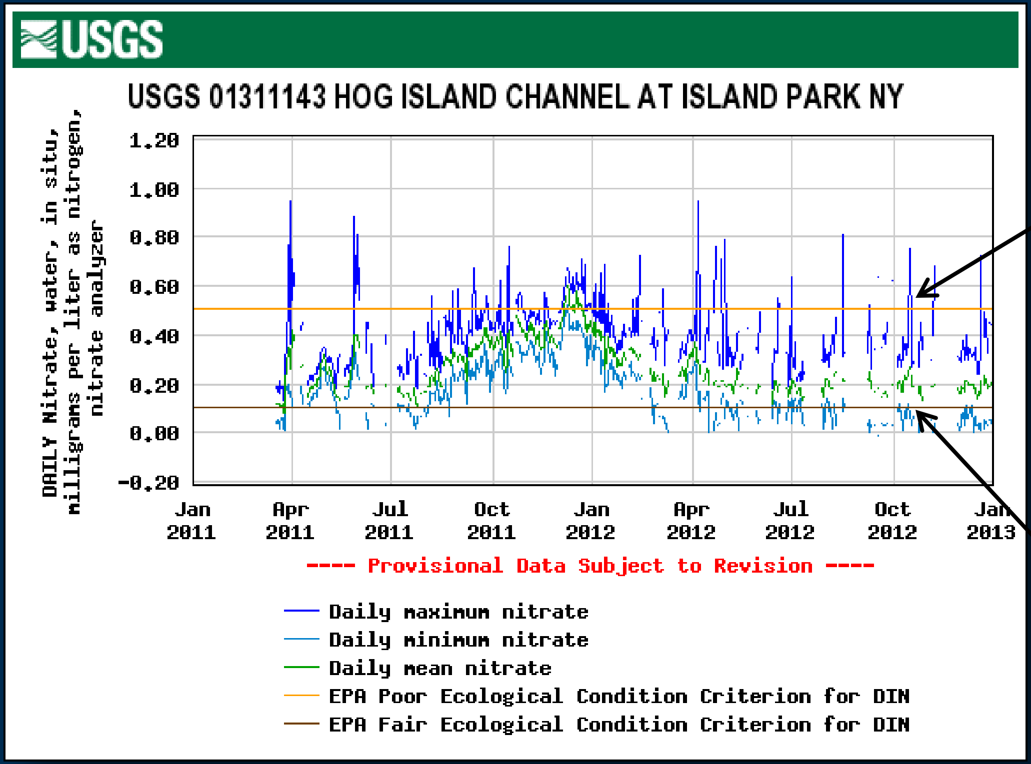
# Evaluating Ecological Condition

Daily statistics show fair to poor water quality & ecological condition at mid-bay location




Dick Cartwright, USGS, NY

**Daily mean nitrate** rarely exceeded EPA Poor Ecological Condition Criterion for DIN (>0.5 mg/L as N)

**Daily mean nitrate** sometimes remained below EPA Fair Ecological Condition Criterion for DIN (0.1 mg/L as N)

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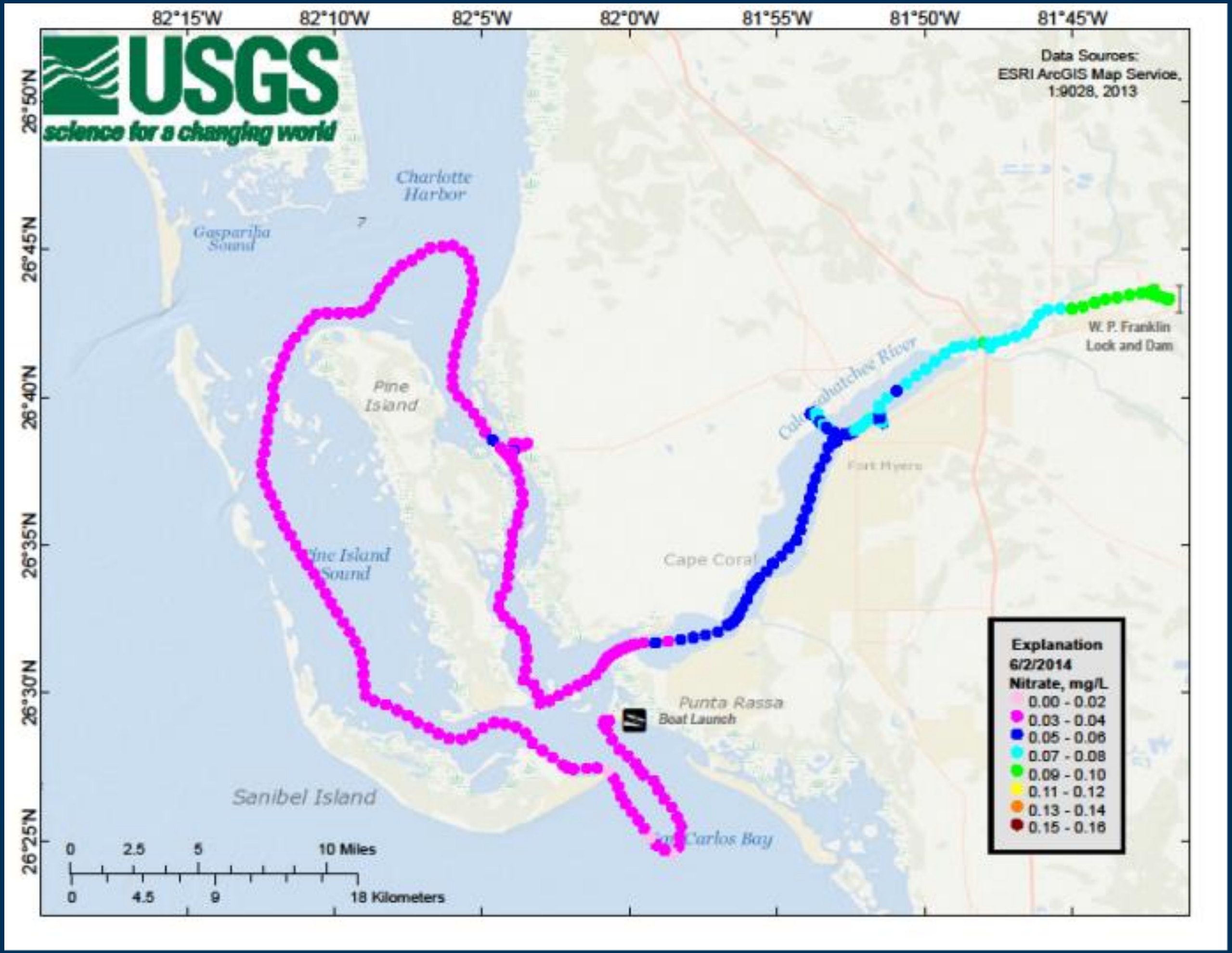
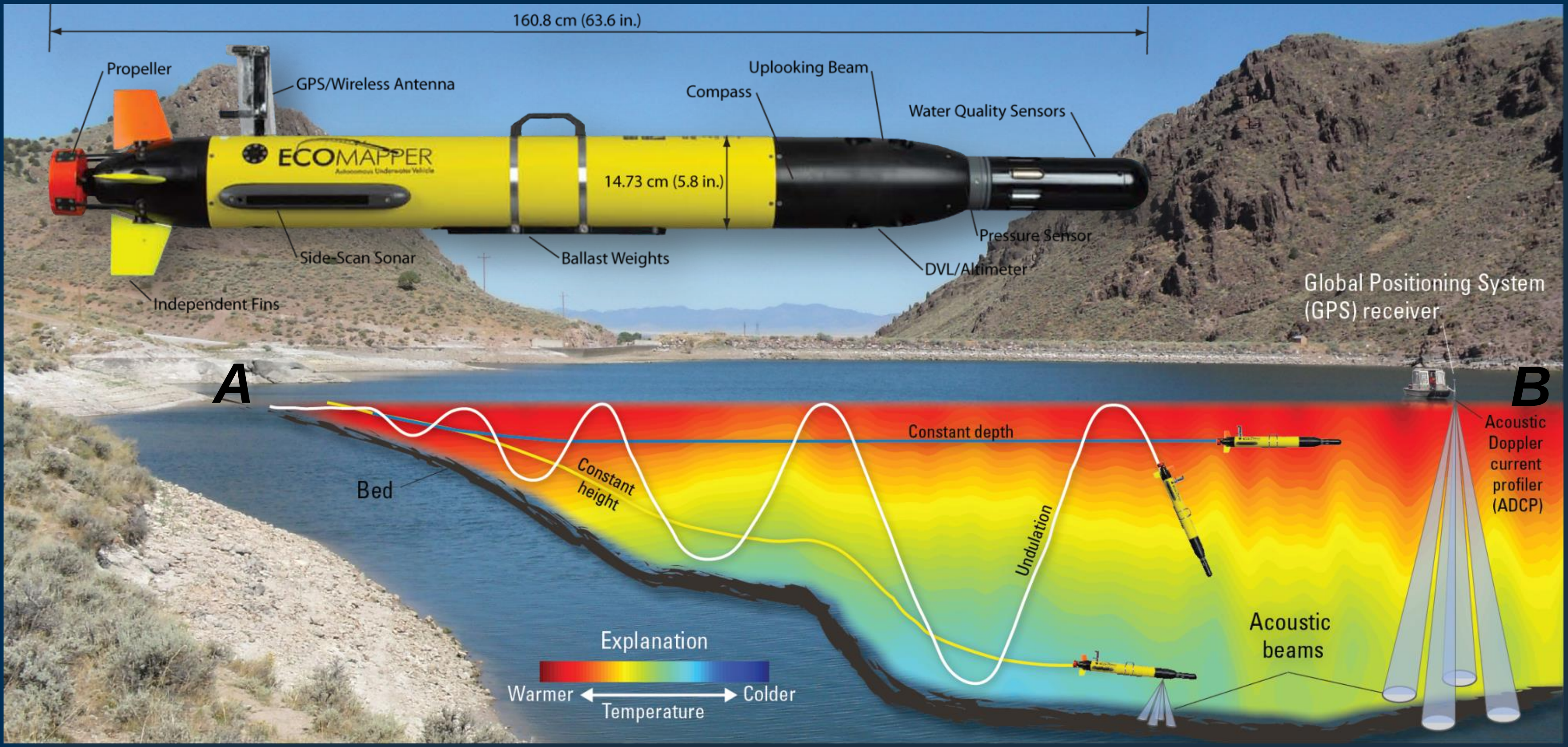
# Moving Boat Surveys

Spatial mapping to identify hot spots (sources or sinks), mixing, etc.




Amanda Booth, USGS, FL

# Autonomous Underwater Vehicle Surveys




Newcastle Reservoir, Utah

Ryan Jackson, USGS, IL Water Science Center

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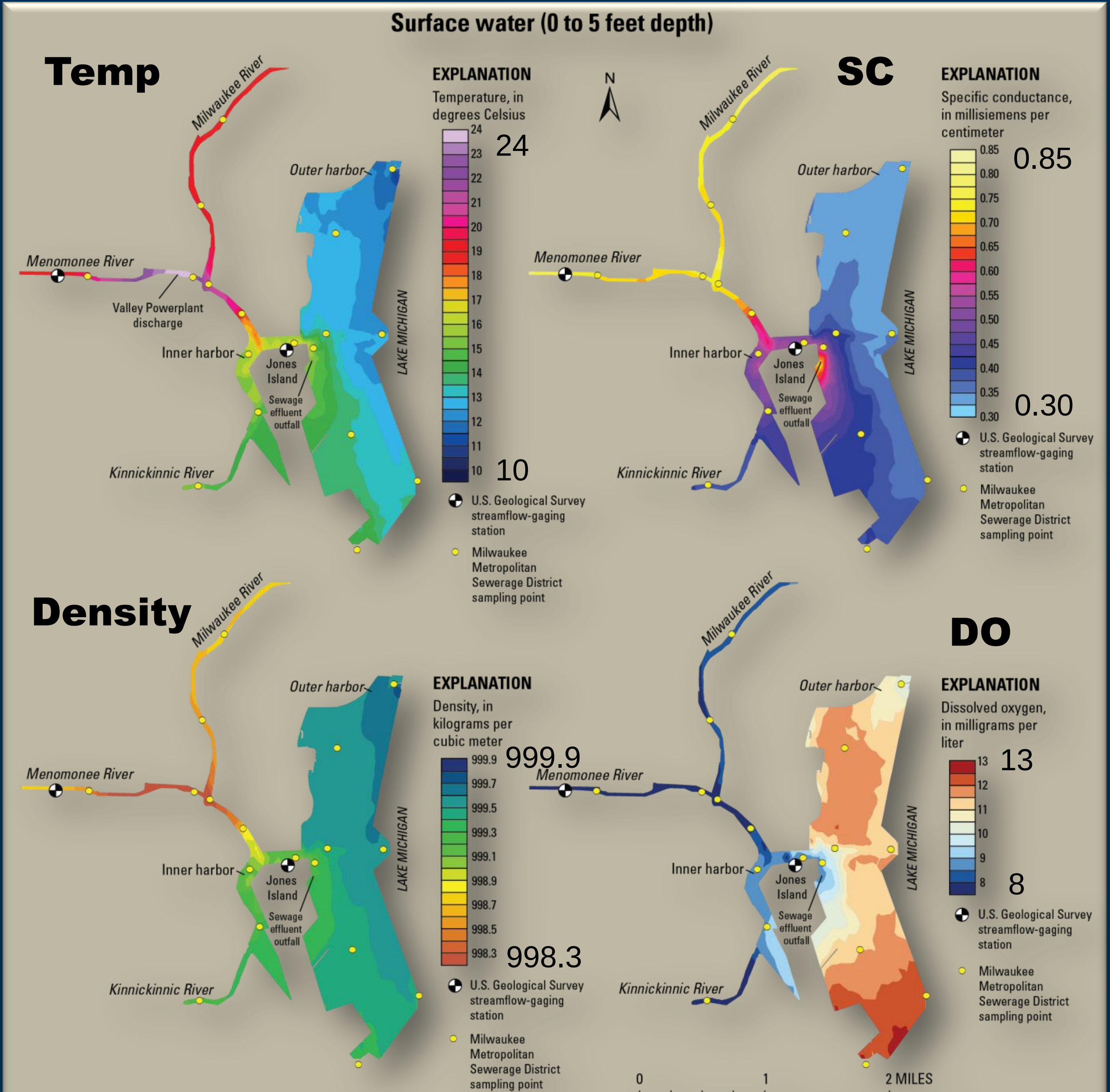
# Milwaukee River Estuary, Milwaukee, WI

## September 7-9, 2010




(Ryan Jackson, USGS, IL)

From:
Jackson and Reneau
USGS SIR 2014-5043

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# The (Near) Future

If you don't know where you're going, you might not get there.” – Yogi Berra

# New Protocols and Guidelines

Key to an accurate, comparable, real-time data

Examples:

- National Water Quality Monitoring Council (NEMI, Sensor Workgroup, …)
- USGS Techniques and Methods Reports

**USGS Techniques and Methods Report** on in situ fluorometers (to be published in 2015) will include:

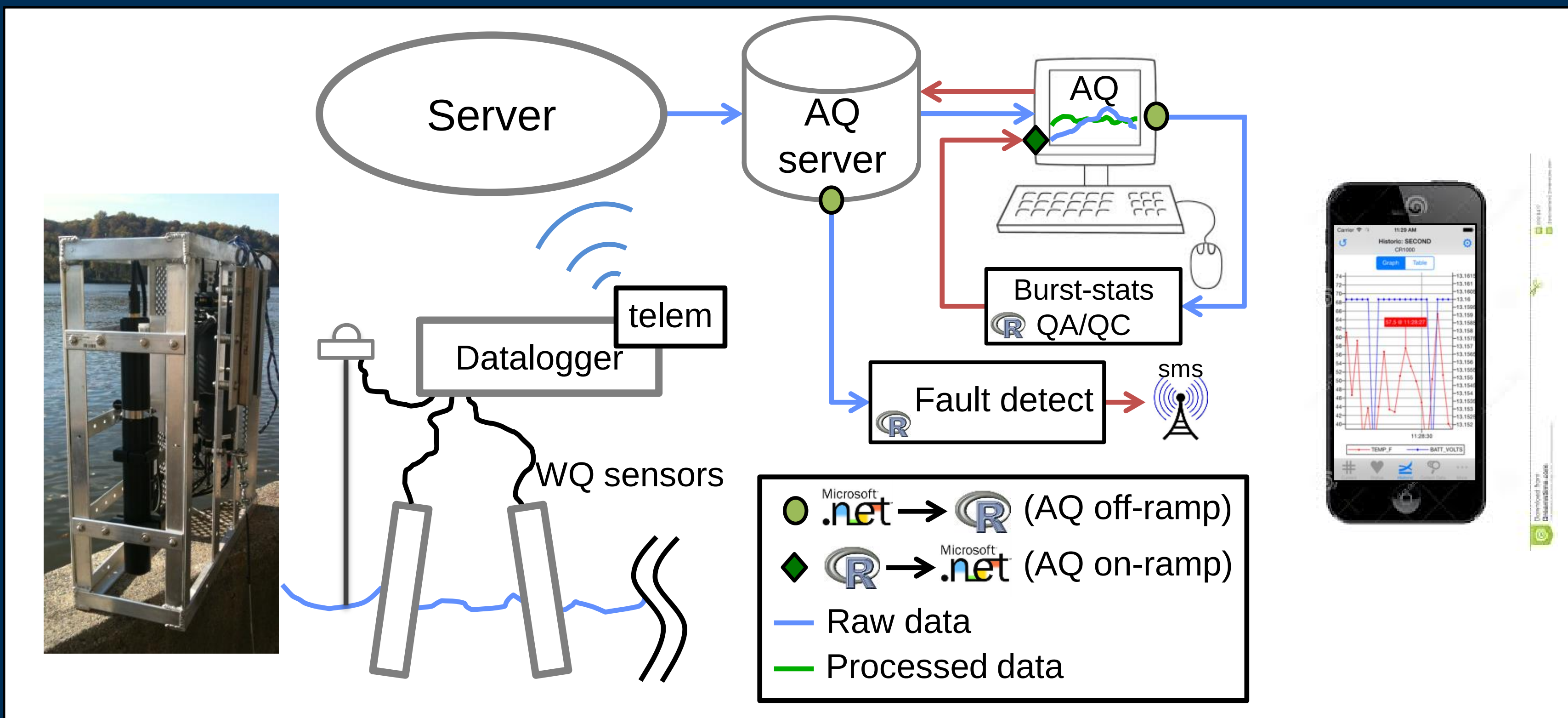
- Matrix interferences
- Sensor calibration and validation
- Environmental variability
- Units
- …

Matrix effects on fluorometers


USGS

# Lower Cost, Easier to Use, More Efficient

- “Plug-and-play” integration for sensors
- Remote communication through phones and tablets
- Automated QAQC and metadata with new databases
- Partnerships with manufacturers (e.g. Nutrient Sensor Challenge)



# Nutrient Sensor Challenge

- In partnership with the Alliance for Coastal Technologies (ACT), Challenging Nutrients is developing the **Nutrient Sensor Challenge** (www.nutrients-challenge.org)
- **Goal:** Accelerate development and commercial availability of affordable, reliable, and accurate *in situ* nutrient sensors
- **Incentives:** Testing/verification, publicity, recognition, market access
- How you can **be involved**:
  - Visit the website and indicate your support and/or interest.
  - Email info@nutrients-challenge.org for more information

# Expand Applications

- Surface water
- Groundwater
- Edge-of-Field
  - Get out of the stream and on the landscape where runoff is directly affected by field practices
  - Reduce influence of “in stream” processes
  - Inform BMPs

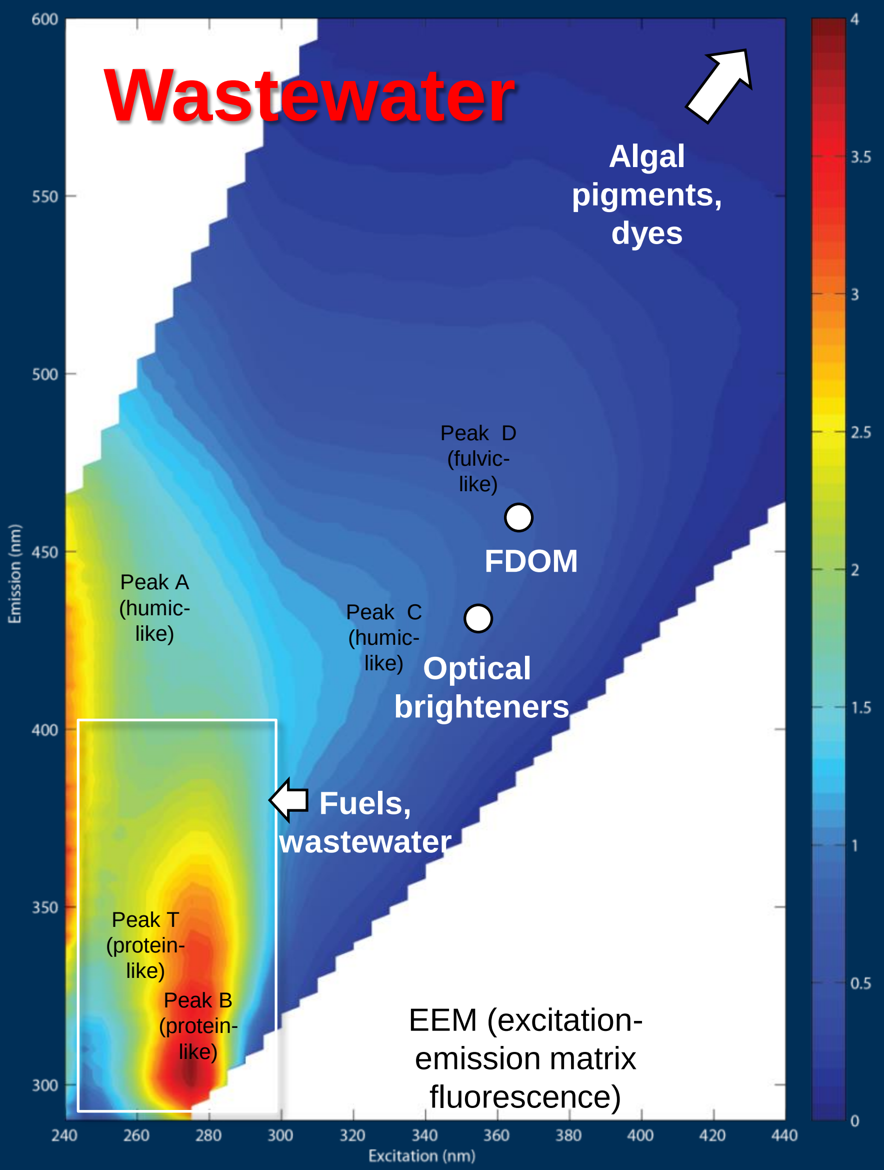

**GLRI Priority Watersheds**
(Matt Komiskey, USGS, WI)

Tulane University's Grand Challenge "Water Innovations:  Reducing Hypoxia, Restoring Our Water" will seek technical market based solutions to combat hypoxia, a deadly deficiency of oxygen in water created by the excessive growth of phytoplankton. http://tulane.edu/tulaneprize/waterprize/

# Next Generation Sensors

From "proof-of-concept" to "field ready":

- **Low UV fluorometer**
  - Target low UV fluorescence as unique indicator of wastewater presence
  - Indicators for the potential presence of pathogens and bacteria
- **Algal taxa**
- **Sediment size**
- **Ammonia**
- **DNA**
- **…**




(Steve Corsi, USGS, WI)

# National Networks

How would we build nationally-consistent, real-time, continuous nutrient monitoring network thats:

1. Meets monitoring needs (drinking water quality, TMDLs, edge-of-field loads, coastal issues)
2. “Accelerates the pace of discovery” (*White House Big Data Research and Development Initiative*)
3. Has some long-term “stability”
4. Improves our efficiency (from data collection to decision support)?

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CHARGE: Where will time dense nutrient data change what you know or what you do about water quality?
Thanks!
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